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TEST AND EVALUATION OF AN ENERGETICS SCIENCE INCORPORATED MODEL--ETC(U)
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TEST AND EVALUATION OF AN ENERGETICS SCIENCE INCORPORATED MODEL 7660 ELECTROCHEMICAL HYDRAZINES ANALYZER

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USAF SCHOOL OF AEROSPACE MEDICINE Aerospace Medical Division (AFSC) Brooks Air Force Base, Texas 78235



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NOTICES

This final report was submitted by personnel of the Crew Environments Branch, Crew Technology Division, USAF School of Aerospace Medicale, Aerospace Medical Division, AFSC, Brooks Air Force Base, Texas, under job order 7930-11-36.

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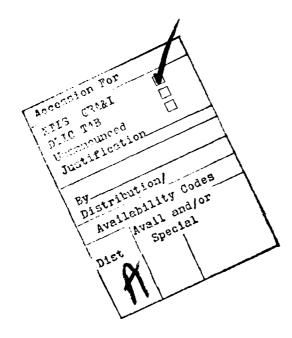
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20. ABSTRACT (Continue on reverse side it necessary and identity by block number) An Energetics Science Incorporated Model 7660 MMH at ated for continuous real-time measurement of Hz, MMH tivity to the hydrazines was approximately 0.06 ppm ppm UDMH. Accuracy and precision, determined at 0.1 analyzer calibrated daily, were between 20% and 40% Analyzer response time increased with age (use) of analyzer operation, the time for 90% of final response	I, and UDMH in air. Sensi- Hz, 0.04 ppm MMH, and 0.025 I-ppm concentrations on an for the three hydrazines. The sensor. At 100 hours of
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20. ABSTRACT (Continued)

MMH; and 1 min, UDMH. Interference studies showed the analyzer responding strongly to ammonia and hydrogen sulfide and less strongly to alcohols and amines. There was also interference from simulated spills of hydraulic fluid, JP-4 fuel, and ECS fluid, with relative analyzer response as high as 6 ppm MMH in the spill area. Interference and response-time problems prevent the analyzer, with the presently used liquid sensor, from being satisfactory for monitoring at or below the threshold limit values for any of the three hydrazines. The instrument is satisfactory for use as a low-ppm leak detector if precautions are taken for distinguishing between the hydrazines and interferents.



TEST AND EVALUATION OF AN ENERGETICS SCIENCE INCORPORATED MODEL 7660 ELECTROCHEMICAL HYDRAZINES ANALYZER

INTRODUCTION

The Air Force uses hydrazine (Hz), monomethylhydrazine (MMH), and unsymmetrical-dimethylhydrazine (UDMH) for rocket motor fuels. All three hydrazine compounds are toxic and highly reactive. Threshold limit values (TLV), which are time-weighted average exposures for an 8-hour workday, were established by the American Conference of Governmental and Industrial Hygienists (ACGIH) at 0.1 ppm Hz, 0.2 ppm MMH, and 0.5 ppm UDMH. Adoption of the ACGIH values as Air Force Occupational Safe 3 and Health (AFOSH) standards has resulted in Air Force testing and development of instruments and methods for monitoring airborne concentrations of the three hydrazines at 100% to 10% of the established TLVs.

The subject of this report is the test and evaluation of an electrochemical hydrazines analyzer (Ecolyzer, Model 7660, S/N BAFB-1) manufactured by Energetics Science, Inc. (ESI) of Elmsford, New York. This analyzer-the result of a NASA/Navy [5] effort to develop a portable instrument for measuring trace MMH concentrations in air--represents the state-of-the-art at time of purchase in early 1979. A prototype (Model 7000) analyzer had been evaluated by the Naval Research Laboratory (NRL) [8]; and a somewhat smaller, less sensitive version, called the Hipster, had been investigated and evaluated by a group at NASA [1]. Both evaluations were concerned mainly with MMH measurement. The objective of this study was to provide an independent evaluation, to expand on the NRL and NASA studies by extending testing to Hz and UDMH, and to make a more in-depth investigation of instrument sensitivity and potential chemical interference.

BACKGROUND

The Ecolyzer is a dual-channel instrument, actually two instruments in one, with both channels used for measuring MMH. Each channel is physically separate and has its own air pump, flow control system, and electrochemical sensor (Fig. 1). Both channels incorporate the same high and low measurement range, 0-20 ppm and 0-2 ppm respectively, with an analog meter providing readout. Minimum detectable concentration for the instrument is stated by the manufacturer as 0.020 ppm MMH. The Ecolyzer is a portable unit measuring approximately 20 x 20 x 40 cm, weighs less than 8 kg, and operates in either battery (DC) or AC mode.

The principle of instrument operation is electrochemical, with reactions carried out in an aqueous-base electrolyte system at potential-controlled diffusion electrodes. An air sample is pumped at a controlled flow rate of about

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400-500 ml/min over the back (gas) side of a sensing electrode (a catalyzed Teflon-bonded diffusion type). MMH in the air sample diffuses across the sensing membrane to the catalytic site where electrochemical oxidation takes place. The oxidation results in a current flow between sensor and counter electrode, which is amplified and displayed on the direct reading panel meter. Meter readout is in ppm of MMH (0-2 and 0-20 ppm full scale). Provision is made for attaching a recorder if necessary. A reference electrode is used in the Ecolyzer for operation of the potentiostats.

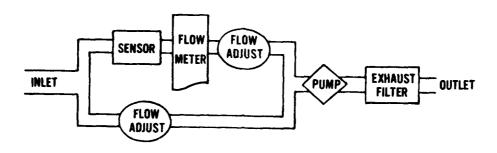


Figure 1. Schematic of ESI Model 7660 MMH electrochemical analyzer.

EXPERIMENTAL

Hydrazine vapor was generated, diluted, and delivered to the Ecolyzer and test equipment (Fig. 2) by a vapor pressure-diffusion method described in a previous study [3]. Basically, a very low flow of nitrogen (Matheson, high purity) was bubbled through a flask containing pure liquid Hz, MMH, or UDMH maintained at an accurately known temperature. Air (Matheson, zero grade) was mixed with the hydrazine-nitrogen stream to provide air samples of low hydrazine fuel concentrations (0.02-20 ppm) at flow rates between 1 and 35 liters per minute. These hydrazine-in-air standards were delivered (1) through a glass manifold to the Ecolyzer for test and evaluation, (2) to a breadboard chemiluminescent hydrazine analyzer [4] for real-time measurement, (3) intermittently to a line tap to provide a sample for analysis of Hz and MMH by the para-dimethylaminobenzaldehyde [7] or of UDMH by the trisodium pentancyanoaminferrate [6] colorimetric methods, and (4) with excess to vent to avoid pressurization and other insult to the sampling system of the analyzers. Most of the flow system was made of glass that was heated at critical points to prevent absorption and condensation of the hydrazines on apparatus walls.

Contaminants for testing were prepared as vapors in air by injecting an accurately measured amount of pure gas or liquid into an evacuated high pressure cylinder. Air was added to the cylinder to the proper dilution (pressure) desired. Prepared sample concentrations were verified by infrared spectroscopy (Miram Model 1A or Perkin-Elmer Model 580) using a 20-meter-pathlength gas cell.

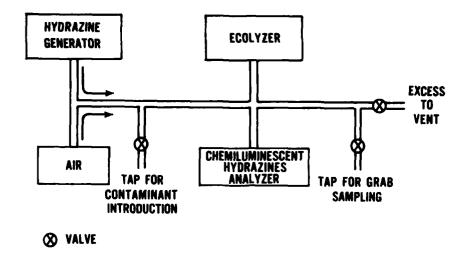


Figure 2. Schematic of test apparatus.

RESULTS AND DISCUSSION

Instrument Function

The Ecolyzer evaluated was operated for a 3-month period on an 8-hour 5-day-a-week basis. Calibration, using a 2.0-ppm-MMH-in-air standard gas mixture and using zero grade air (instrument zero), was checked daily. In general, span and zero setting changes were not needed over a 2- to 3-day operating period (8 hours per day) and even then required only a small adjustment. Quantitatively, span and zero drift over an 8-hour day, using recorder output, was 3-4% less than the 10% estimated and reported in reference 5.

The only major mechanical problem obtained during the study was failure of one of the sampling pumps. This pump was replaced with a spare we had on hand because of similar problems experienced with servicing the CO and NO_{X} Ecolyzer instruments that we use in our field monitoring programs. No electronic problems were experienced.

Instrument response and apparent stability were subject to physical orientation; no problem occurred in the laboratory because the instrument was not moved or handled very often.

Sensitivity—Ecolyzer sensitivity to the hydrazines was approximately 0.06~ppm Hz, 0.04~ppm MMH, and 0.025~ppm UDMH. Estimates of sensitivity were made using the panel meter dynamically calibrated with the standardized MMH air mixture over the 0-2~ppm range.

Using a recorder rather than the panel meter, changing gain settings on the instrument, and expanding recorder output showed that the Ecolyzer could be used as is in a more sensitive mode. For example, 0.04 ppm MMH measured at a higher gain (factor of 5) resulted in the recorder trace illustration (Fig. 3). Concentrations less than 0.01 ppm MMH could be estimated in this manner, with corresponding sensitivities of 0.015 ppm Hz and 0.006 ppm UDMH possible. However, because of interference, noise, and response-time problems (data to follow), these lower concentrations probably could not be accurately and reproducibly estimated under field monitoring conditions. Even more important, the potential for false alarm and attendant problems is extremely high. The sensitivity values given are in close agreement with manufacturer's claims, are more realistic and usable, and were used as the baseline-reference point for this study.

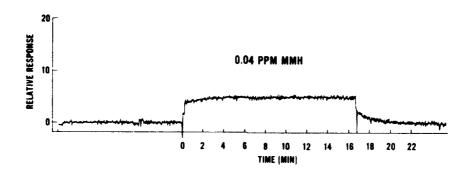


Figure 3. Recorder trace of 0.04 ppm MMH in air with full span expanded to 0-0.2 ppm.

Linearity--Response of the Ecolyzer to all three hydrazines was linear with concentration over the range of 0-20 ppm (Fig. 4). Response ratios for UDMH:MMH:Hz were in the order 1.6:1:0.65. Literature reports [8] on a precursor electrochemical sensor system indicated the reverse order of sensitivity, but personal communication with the authors proved the report to be in error and that the order is as stated herein.

Accuracy and Precision--Hz, MMH, and UDMH concentrations in air delivered to the Ecolyzer were verified by sampling/colorimetric methods that have an accuracy and precision of about 5%. Results of repeated Ecolyzer measurement of trace Hz, MMH, and UDMH concentrations showed a coefficient of variation of about 5% at 1 ppm and 20-40% at 0.1 ppm when Ecolyzer response was compared with colorimetric analysis (Table 1). This reproducibility indicates relatively good accuracy and precision since it includes the built-in uncertainty in concentration of the hydrazines delivered to the analyzer. Accuracy and precision, in this instance, were determined using the recorded traces and do not reflect somewhat larger error inherent in using the meter readout.

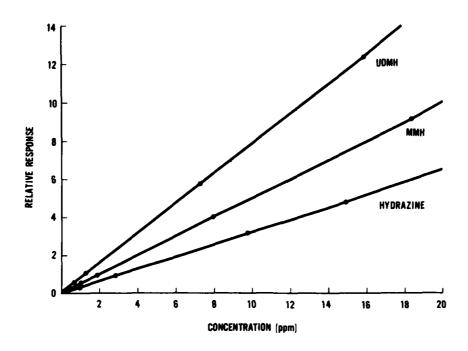


Figure 4. Plot of Ecolyzer response versus hydrazine concentration in air.

TABLE 1. REPRODUCIBILITY OF ESI MODEL 7660 HYDRAZINE ANALYZER RESPONSE TO 1 AND 0.1 PPM CONCENTRATIONS OF THE HYDRAZINES IN AIR

Hydrazine	No. Observations	Concentration (ppm)	
		Colorimetric method	Ecolyzer
Hz	8	1.00 ± 0.05	1.00 <u>+</u> 0.05
	8	0.10 ± 0.01	0.10 ± 0.04
MMH	6	1.00 ± 0.05	1.00 ± 0.05
	6	0.10 ± 0.01	0.10 ± 0.03
UDMH	6	1.00 ± 0.05	1.00 <u>+</u> 0.03
	6	0.10 + 0.01	0.10 <u>+</u> 0.02

Response and Washout Times--Typical recorder traces for Hz, MMH, UDMH, and Aerozine 50 (a 50/50 mix of Hz and UDMH) are illustrated in Figures 5-8. Aerozine 50 was included in the testing because of present interest in monitoring this fuel mixture at Titan missile sites. Table 2 lists typical times required for the Ecolyzer to reach 90% of its final reading (response) and for the return to baseline (washout) after exposure to the hydrazines and Aerozine 50 at various concentrations.

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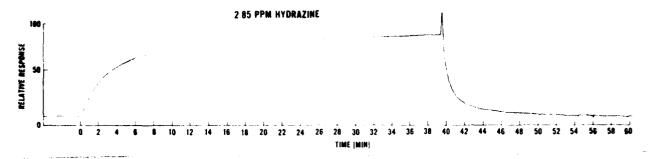


Figure 5. Recorder trace for 2.85 ppm hydrazine in air (using ESI Model 7660).

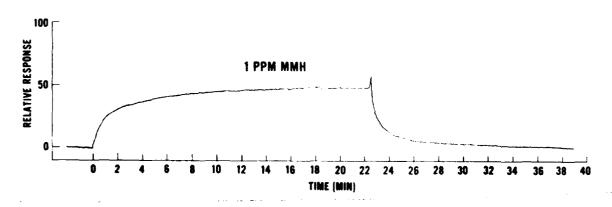


Figure 6. Recorder trace for 1.0 ppm MMH in air (using ESI Model 7660).

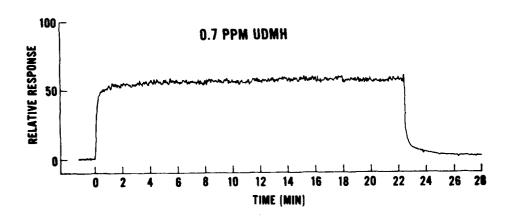


Figure 7. Recorder trace for 0.7 ppm UDMH in air (using ESI Model 7660).

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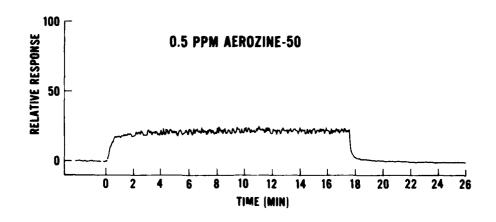


Figure 8. Recorder trace for 0.5 ppm Aerozine 50 in air (using ESI Model 7660).

TABLE 2. RESPONSE AND WASHOUT TIMES FOR ECOLYZER (ESI MODEL 7660) UPON EXPOSURE TO HZ, MMH, UDMH, AND AEROZINE 50

<u>Hydrazine</u>	Concentration	Response (min)	Washout (min)
Hz	0.95	16	35
	2.85	18	20
	9.80	9	14
MMH	1.00	8.5	14
	1.86	6.0	14
	7.80	5.5	13
UDMH	0.70	1.0	0.8
	1.30	1.0	7
	7.30	0.8	10
Aerozine 50	0.5	1.0	1.0

Observed response times are not in compliance with design specifications (90% of final concentration in 90 seconds) for the ESI Model 7660 MMH analyzer. Comparison of Figure 3 (MMH response time at a concentration of 0.04 ppm which satisfies design requirements) with its counterpart, Figure 6 (unsatisfactory response time), points to a sensor-cell aging problem. The quick response to 0.04 ppm MMH was obtained with a sensor that had been operated for less than 30 hours. The Figure 6 trace and Table 2 data were obtained after the instrument had been operated for 100 hours or more and had seen numerous loadings of the three hydrazines. An accurate log of operating time for each sensor was not maintained; therefore, a detailed study of sensor response-time degradation was not cataloged. However, even with the limited information given above, we see that a simple quality test made on a new sensor might not

indicate the same performance level as would be indicated after as little as 50 hours of operating time. The question of what effect sensor aging has on response time could be further complicated by the history of sensor use. That is, is degradation of response and washout times affected simply by evaporative loss of water from the sensor electrolyte, or is it also affected by the accumulative total of hydrazines and other contaminants seen by the sensor? Possibly both effects and other considerations are important.

Instrument Specificity--Ecolyzer response to various chemical interferents was tested using pure compounds and commonly found complex mixtures (for example, engine exhaust) expected in environments to be monitored. Interferents were not mixed with hydrazine standards for testing; only interferent response was sought. Table 3 is a summary of the interference testing results. Compounds tested included amines; alcohols; aliphatic, olefinic, and aromatic

TABLE 3. DATA FROM INTERFERENCE TESTING OF ECOLYZER, ESI MODEL 7660

Interferent	Hydrazine analyzer concentration tested (ppm)	Response as % MMH	Concentration (ppm) to give 0.1 ppm MMH response
Ammonia	5	36	0.3
Methylamine	50	6.4	1.6
Di ethylami ne	32	2.8	3.6
Aniline	36	1.3	7.8
Methanol	50	7.6	1.3
Ethanol	18	4	2.5
iso-Propanol	43	1.6	6.3
Hexane	8	No response	No response
Ethylene	50	0.2	50
Benzene	9	No response	No response
Acetone	30	2	5
H ₂ S	7	120	0.09
so ₂	50	8	1.2
NOx	10	-0.04	Not applicable
CO	50	0.1	100
Freon 114	50	No response	No response
Methylene chlo	oride 30	2.5	4

halogenated hydrocarbons; aldehydes; ketones; organic sulfides; and common air pollutants such as sulfur dioxide, nitrogen oxides, and carbon monoxide. Of the compounds tested, ammonia and hydrogen sulfide showed extremely strong interference. A typical response curve for a 5-ppm-ammonia concentration is shown in Figure 9. Ammonia concentrations in air were verified using a solid-sorbent sampling method followed by Nessler analysis [9]. Hydrogen sulfide proved to be the most sensitive compound tested, producing a response greater than that of MMH (Fig. 10). Other sulfides (e.g., ethylsulfide) also gave rather large responses (80% of MMH response). Most of the listed potential interferents produced a low-level Ecolyzer response, which could cause a false positive in certain applications. This lack of instrument selectivity was brought to our attention by a large fluctuating background signal during early stages of testing. We subsequently determined that the signals were caused by the acetic acid reagent used in the Hz and MMH analytical verification procedure.

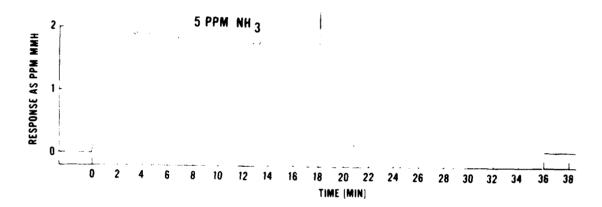


Figure 9. ESI Model 7660 response to 5 ppm ammonia in air.

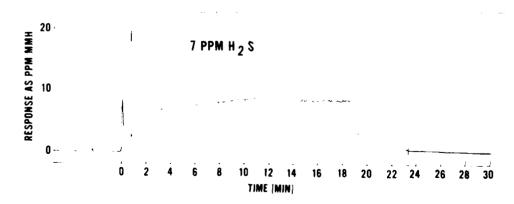


Figure 10. ESI Model 7660 response to 7 ppm H_2S in air.

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Some complex mixtures that could contribute to interference problems were investigated in a semiquantitative manner. Cigarette smoke directed toward the analyzer sample inlet, for example, caused an off-scale spike on the 0-20-ppm range; return to instrument zero took about 30 minutes (Fig. 11). Internal-combustion-engine exhaust had little effect on the analyzer unless the sample inlet was located close to the exhaust outlet. Military fluids such as Mil 7808 turbine-engine lubricating oil gave no response. Mil 5606 hydraulic fluid, JP-4 fuel, and Coolanol 25R (an aircraft heat-exchange fluid) spills caused Ecolyzer response as high as 6 ppm MMH (Fig. 12) in the vicinity of the spill.

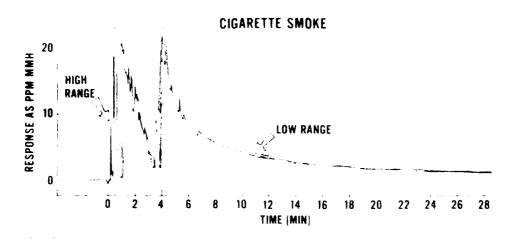


Figure 11. ESI Model 7660 response to cigarette smoke blown into the vicinity of the analyzer's sample inlet (high range 0-20 ppm MMH; low range 0-2 ppm MMH).

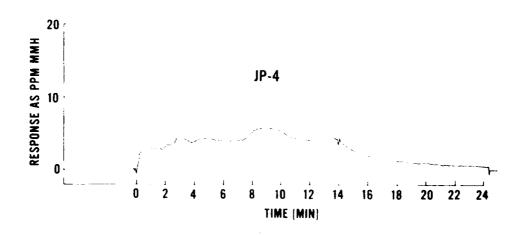


Figure 12. ESI Model 7660 response to JP-4.

CONCLUSIONS AND RECOMMENDATIONS

The Ecolyzer, ESI Model 7660, is not recommended for use as a continuous real-time TLV monitor for Hz, MMH, or UDMH. This recommendation is based on Ecolyzer performance under laboratory conditions and does not take into account field-use considerations, such as temperature, reliability of parts, ruggedness, and maintainability.

In the absence of chemical interference, instrument sensitivity was satisfactory at the TLV level for all three hydrazines. However, because of the quantitated lack of instrument specificity, it is unlikely that the instrument can be trusted (expected high frequency of false alarms) for routine monitoring at these low hydrazine-fuel concentrations. Since chemical interference rapidly becomes less of a problem at less sensitive instrument settings, the instrument would be useful as is for leak-detection monitoring of concentrations above the TLVs (probably at minimum detectable concentrations on the order of 2-5 ppm).

Since completion of testing, the instrument manufacturer [10] has acknowledged many of the deficiencies discussed here and has provided us with a recently developed improved sensor that will be incorporated in a new-generation instrument. We will install the improved sensor, based on an alkaline gel electrolyte, in the Model 7660 and test it against the same criteria as used here. When the new version of the Model 7660 is available in early 1980, we will obtain and test it. The new sensor and instrument for real-time continuous TLV monitoring will be evaluated in early 1980 and results published as a USAF School of Aerospace Medicine Technical Report.

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